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ScienceDirect

Catalysis Today 125 (2007) 24–28

CATALYSIS TODAY

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A microstructured reactor based *in situ* cell for the study of catalysts by X-ray absorption spectroscopy under operating conditions

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Abstract

In situ X-ray absorption spectroscopic studies have been performed at the silver K-edge, of a silver catalyst deposited in a microstructured reactor cell at operating conditions. Oxidative dehydrogenation of methanol to formaldehyde was performed at atmospheric pressure and 773 K with a feed containing 9.7% CH_3OH, 18.8% O_2 (N_2 as balance) at residence time of ~10 ms. The as-prepared catalyst shows that only metallic silver phase is present. Analysis of the EXAFS data recorded during calcination at 773 K in air, indicates that some of the silver metal catalyst is oxidised. Upon introduction of methanol/air mixture, part of the oxygen coordination is removed suggesting that an oxidation/reduction cycle takes place during the reaction. This work demonstrates that such microfabricated reactors can be readily used for *in situ* X-ray absorption spectroscopy.

Keywords: XAS; XANES; EXAFS; Microstructured reactor; Silver; Methanol; Formaldehyde

1. Introduction

Metals and supported metal catalysts belong to a family of heterogeneous catalysts, which are routinely used in several reactions. It is well recognised that efficiency of the catalyst, longevity and performance are related to the nature of active sites, intrinsic reactivity and in general the structure of the catalytic system. A variety of techniques are used to determine the structure of the catalysts and among them X-ray based techniques provide direct means of obtaining the atomic-architecture of catalytic materials [1–12]. Other spectroscopic techniques, in particular Raman spectroscopy, is useful in determining catalytic species and reaction intermediates [13–17]. Although X-ray diffraction is a powerful technique to determine the structure of catalysts, often due to large disorder and amorphous nature of the catalytic material, it is difficult to determine the structure of the catalytic solids by this technique. X-ray absorption spectroscopy (XAS), which consists of X-ray absorption near edge structure (XANES, which provides geometric, electronic and chemical state information) and extended X-ray absorption fine structure (EXAFS, which provides local geometric structure information) is now routinely used to determine the structure of disordered, poorly crystalline and amorphous catalytic materials. This technique does not depend on long-range arrangement of the atoms and it is atom-specific [2–4,7–10,12]. Although, several *in situ* methods have been developed to study catalytic materials by X-ray absorption spectroscopy, there is still a continued interest in developing new methods, in particular for studies at operating conditions.

In recent years, microstructured reactors have been utilized for the study of heterogeneous catalytic reactions [18,19]. With reaction channels down to few microns to hundreds of microns in dimension, microstructured reactors can offer distinct advantages [20,21]. The microscale dimensions result in low transport resistances such that heat and mass transfer are extremely fast and equilibration is nearly instantaneous both thermal and compositional. The small diameters of the reaction channel ensure precise control of residence time. In addition, the small amounts of reactants required minimize danger when using toxic or explosive chemicals. Catalyst materials can be

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doi:10.1016/j.cattod.2007.01.068

coated on the channel walls by a number of methods including sputtering, evaporation, sol–gel or slurry wash-coating, while solid catalysts can be packed into microreaction channels to form packed-bed microreactors. Therefore, microstructured reactors are ideal for investigating catalysts under operating conditions. Recently, some of us demonstrated that *in situ* Raman spectroscopic studies are possible using microstructured reactors [22]. There are reports presenting the use of microchannel reactors for *in situ* studies using synchrotron radiation techniques, in particular employing small angle X-ray scattering, but for non-catalytic applications [23–25]. In this paper we report the use of microstructured reactors to follow a well-studied reaction over a well-known catalyst, namely the oxidative dehydrogenation of methanol to formaldehyde over silver using X-ray absorption spectroscopy (XAS). The study clearly demonstrates that this reactor system can be effectively used for *in situ* spectroscopic studies to determine changes at atomic level during a catalytic reaction which can be used to derive structure–function relationships.

2. Experimental

In situ XANES and EXAFS measurements were performed at station 16.5 of Daresbury Laboratory, which operates at 2 GeV with a typical current in the range of 150–200 mA. The experimental station is equipped with a Si(2 2 0) double crystal monochromator, ion chambers for measuring incident beam and transmitted beam intensity and a 32 element fluorescence detector (Canberra) for measurements in fluorescence mode. Except for the model system, Ag metal, all the *in situ* measurements were carried out in fluorescence mode, since the microstructured reactor contains a thick glass plate which prevents any transmitted beam through the reactor.

The microstructured reactor used in this work was similar to that described elsewhere [22,26]. It consisted of silicon and glass and was fabricated by photolithography, deep reactive ion etching (DRIE) and anodic bonding. It contained a single microchannel of 8 mm wide and 120 μm deep. A thin film of silver was coated on the reaction channel using a Turbo Sputter Coater (K675XD, Emitech) before anodic bonding. The dimensions of the silver film were 12.5 mm in length and 0.25 mm in thickness. The structured silicon with deposited silver layer was bonded with a 1 mm glass cover with inlet/outlet holes. A picture of the reactor is shown in Fig. 1.

A custom made heating assembly was designed and fabricated which could house the microchannel reactor with appropriate gas inlet and outlet. A schematic arrangement of the reactor and the XAS measurement system is shown in Fig. 1. The system had provision for purging the reactor with nitrogen. In a typical experiment the reactor was placed in the heating

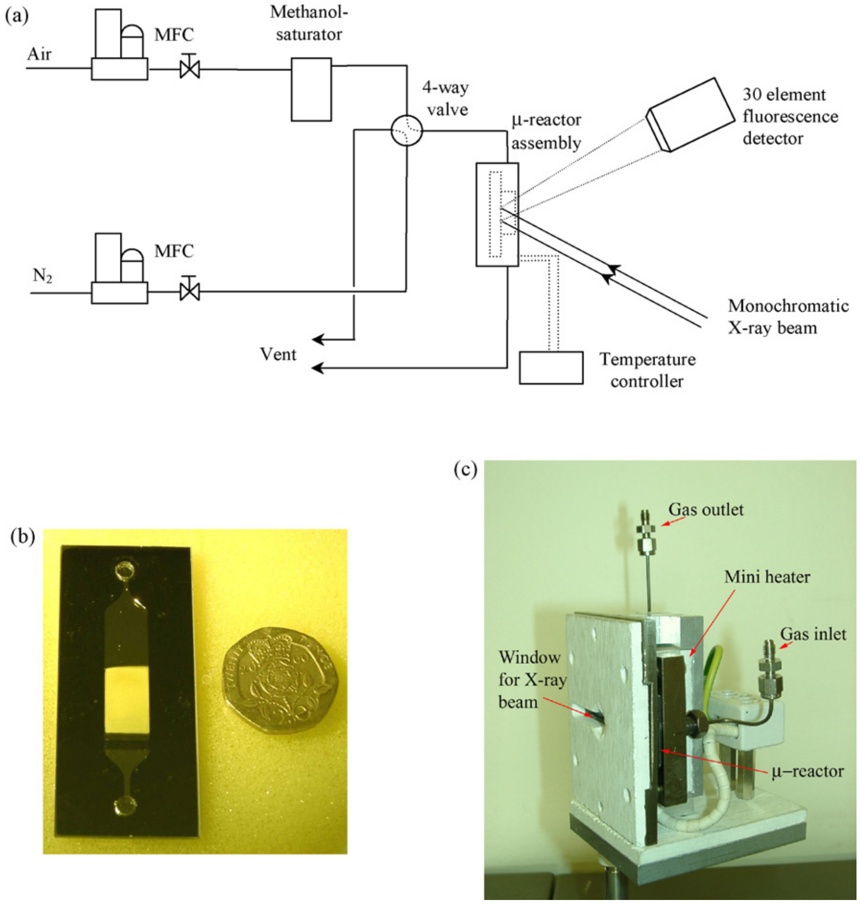

Fig. 1. (a) Schematic diagram of the *in situ* setup used for the X-ray absorption spectroscopic measurements in fluorescence mode. (b) Microstructured reactor. (c) *In situ* cell photographed from the direction of the incident X-ray beam.

assembly and air either passed directly (for calcination) into the reactor or through a CH_3OH saturator to carry a reaction mixture (9.7% CH_3OH, 18.8% O_2, N_2 as balance) into the reactor (for methanol oxidative dehydrogenation). The reactor was mounted in such a way that the X-ray beam penetrated the silicon wafer and the fluorescence coming through the silicon was measured. Typical beam size was about 0.4 mm × 10 mm and this beam was orientated horizontally. Typical data collection time was about 40 min per scan. Measurements were carried out at room temperature, during calcination in air at 473, 773 K and during reaction with methanol at 773 K and residence time of ~10 ms. XANES and EXAFS data were processed using a suite of programs available at Daresbury laboratory, namely EXCALIB, EXBROOK and EXURV98.

3. Results and discussion

In Fig. 2 we compare Ag K-edge X-ray absorption data of Ag foil (10 μm thick used as standard), and of Ag sputtered catalyst inside the microchannel reactor. Both Ag K-edge XAS, XANES, EXAFS and the associated Fourier transform (FT) (see Fig. 2(a–d), respectively) clearly show that there are no artefacts in the data collected through the silicon wafer of the microchannel reactor. The additional peak seen in the FT of the catalyst, in Fig. 2(d), at ca. 2 Å is due to truncation effects which are also present in the calculated EXAFS data and thus it is not related to any scattering.

Table 1
Structural parameters obtained from the detailed analysis of the EXAFS data of sputtered silver catalyst in a microstructured reactor, employing curve-fitting procedures

Temperature (K)	Atom-pair	Coordination number (N)	Distance R (Å)	Debye–Waller factor σ^2 (Å^2)
Room temperature	Ag–Ag	11.6	2.86	0.009
473 in air	Ag–Ag	11.2	2.87	0.014
773 in air	Ag–O	0.6	2.16	0.007
	Ag–Ag	10.0	2.83	0.019
773 in methanol	Ag–O	0.2	2.13	0.007
	Ag–Ag	11.0	2.86	0.017

Fig. 3(a) shows the FT of the experimental EXAFS data (solid line) and the FT of the calculated EXAFS (dashed line) obtained from the curve-fitting analysis (the structural parameters obtained from the analysis are given in Table 1) of sputtered silver catalysts, before and during calcination and the catalytic reaction. The main peak in the FT appearing at ca. 2.86 Å (phase shift corrected) corresponds to the Ag–Ag distance. There is a small peak around 2.2 Å which is due to truncation effects; there may also be some Ag–O contribution. However, introducing Ag–O scattering in the analysis did not produce appreciable improvement to the fit index (measure of the goodness of fit between experimental data and calculated EXAFS using structural parameters listed in Table 1) from the

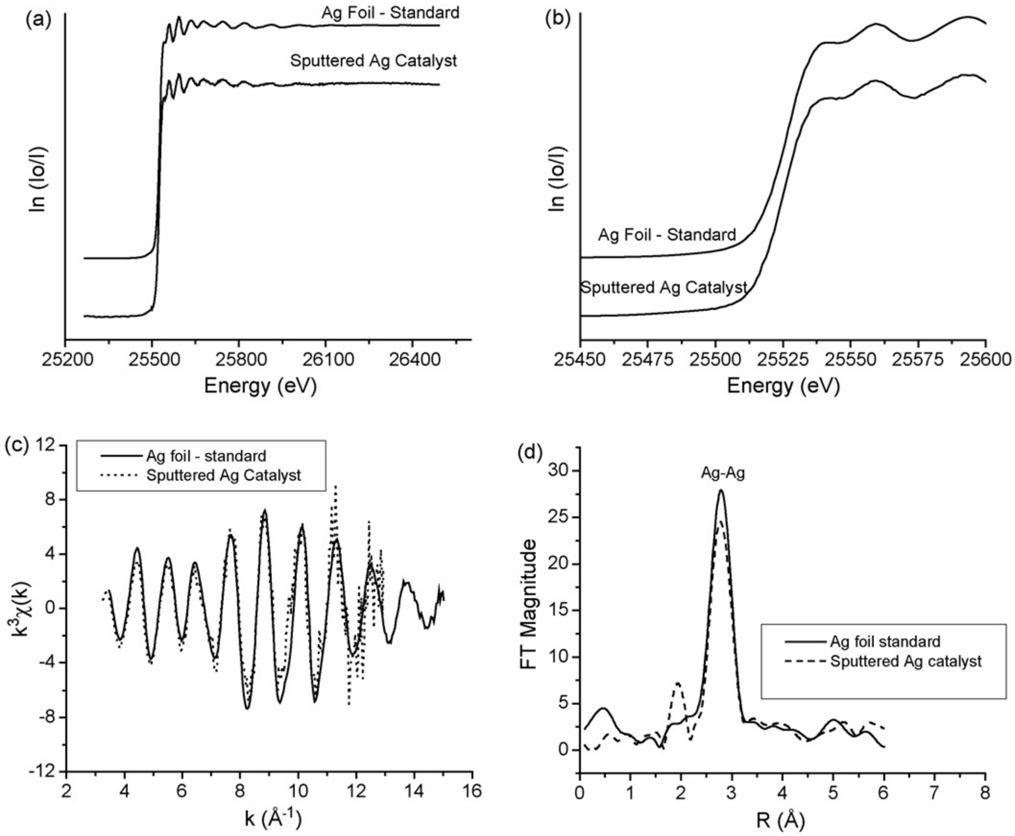

Fig. 2. Ag K-edge X-ray absorption spectroscopic data of a standard 10 μm silver foil, and silver sputtered catalyst in the microreactor. (a) Normalised Ag K-edge XAS data, (b) XANES data, (c) EXAFS data and (d) Fourier transform of the EXAFS data. These measurements were carried out at room temperature.

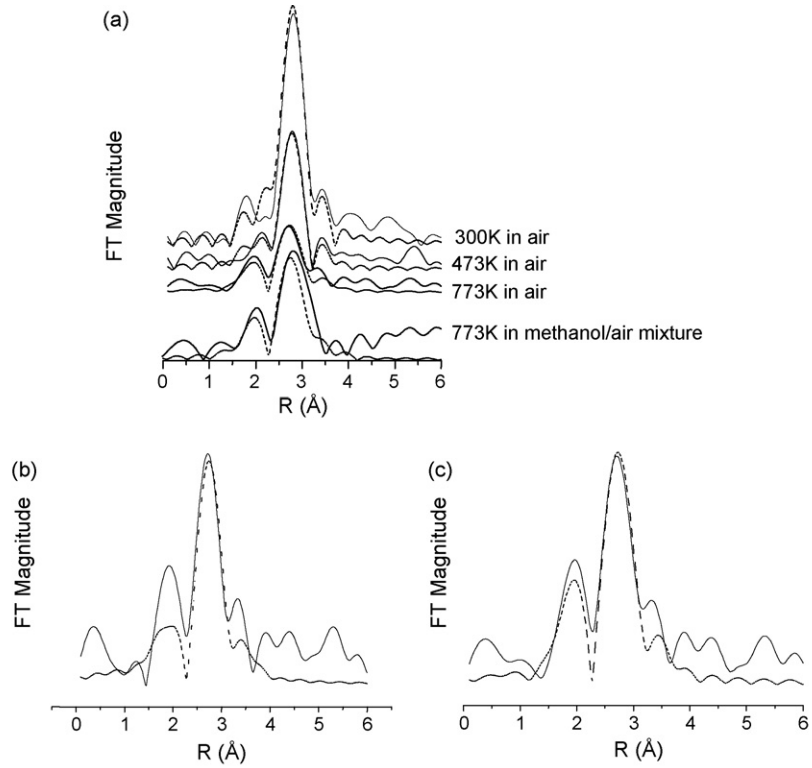

Fig. 3. (a) Fourier transforms of the Ag K-edge EXAFS data of silver sputtered catalyst recorded at room temperature prior to calcination, during calcination at 473 K, during calcination at 773 K and during reaction with methanol/air mixture at 773 K. The solid line shows the FT of the experimental EXAFS data and the dashed line represents the FT of the calculated EXAFS. (b) Comparison of the FTs of the experimental and calculated EXAFS generated using only Ag–Ag scattering. (c) Comparison of the FTs of the experimental and calculated EXAFS generated using contribution from Ag–Ag and Ag–O scattering.

one calculated from only Ag–Ag scattering. Upon heating the catalyst to 473 K in air, the FT of the EXAFS data (see Fig. 3(a) showed a decrease in the magnitude of the Ag–Ag scattering. It is clear from the analysis (see Table 1) that the data collected at 473 K showed an increase in dynamic disorder arising from the high-temperature measurements, which is reflected in the increase in Debye–Waller factor (hence decrease in the magnitude of the FT). Inclusion of additional Ag–O scattering did not improve the quality of the fit, suggesting that only negligible amount of oxide may have formed at these temperatures. The FT of the EXAFS data recorded at 773 K, during calcination in air, clearly showed further decrease in the magnitude of the 2.86 Å peak (see Fig. 3(a)) and also a slight enhancement in the peak at low R distance. In this case, it was necessary to include additional Ag–O scattering to obtain a good fit between experimental and computed EXAFS. Fig. 3(b and c) show the comparison between the FT of the experimental and computed EXAFS data, without (only Ag–Ag scattering) and with Ag–O (in addition to Ag–Ag scattering) contribution, respectively. It is clear from the best fit that there is significant amount of oxide phase present in the catalyst calcined at 773 K. The fit index improved from ca. 50.0 to 46.0 after introducing an oxygen shell in the analysis. However, it is difficult to describe the nature of the oxygen species present in the catalyst based on the EXAFS results alone. Upon introduction of the methanol/air mixture, contribution due to Ag–O appears to decrease slightly and correspondingly the Ag–Ag contribution is seen to increase; the results are shown in Table 1. This suggests that part of the oxidised phase is reduced, indicating a dynamic process involving oxidation and reduction of silver metal during the catalytic reaction. These results are consistent with our previous operando Raman–GC study in an identical reactor [22], where strongly bound atomic oxygen species were detected after pre-treatment of silver in a flow of O_2/He ($O_2 = 4.1\%$) at 773 K with characteristic Raman band at 810 cm^{-1}. These were active in the oxidation of methanol to formaldehyde. With introduction of the reaction mixture (8.75% CH_3OH, 3.5% O_2, 6.63% H_2O with He as balance, residence time 6–7 s), the Raman band at 810 cm^{-1} disappeared, while a broad band appeared at lower Raman shift. The reaction product analysed simultaneously by gas chromatography, showed a considerable conversion of CH_3OH (~75%) with selectivity to formaldehyde at ~80% at these reaction conditions.

In summary, this study demonstrates that microstructured reactors can be used as an effective *in situ* tool for studying catalysts under operating conditions. This method opens further possibilities to combine the powerful X-ray method with other spectroscopic methods, in particular, Raman and UV–vis spectroscopies in addition to monitoring the feed and the reaction product by gas chromatography and mass spectrometry.

Acknowledgements

We thank EPSRC for financial support, CCLRC for provision of beam time and other facilities at Daresbury

Laboratory. We also thank Mr. R.L. Billsborow, Dr. S. Hayama and Dr. S.G. Fiddy for their help and discussions.

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